BIOPOLYMER BASED COMPOSITE MATERIALS FOR THE EXCLUSION OF HAZARDOUS POLLUTANTS

A Synopsis

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Ajay Sharma

(Registration Number: H18IECPHD02)

Under the Supervision of

Dr. Manita Thakur

Assistant Professor

Department of Chemistry

IEC University, Baddi (HP), India

Department of Chemistry

IEC University, Baddi (HP), INDIA

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S.No.	Topic	Page No.
1.	Introduction	1
2.	Literature Review	2
3.	Objectives	4
4.	Research methodology	4
4.1.	Extraction of xyloglucan from tamarind seed	4
4.2.	Synthesis of zirconium(IV) selenophosphate (ZSPT) inorganic ion exchanger	5
4.3.	Synthesis of zirconium(IV) aluminophosphate (ZAP) inorganic ion exchanger	5
4.4.	Synthesis of carob gum based nanocomposite	5
4.5.	Synthesis of xyloglucan based nanocomposite	6
4.6.	Synthesis of carob gum-cl-xyloglucan based composite	6
4.7.	Synthesis of carob gum-cl-psyllium husk based composite	6
4.8.	Ion exchange capacity	7
4.9.	Distribution coefficient studies	7
4.10.	Optical band gap studies	8
5.	Characterization techniques	8
5.1.	Scanning Electron Microscopy (SEM)	8
5.2.	Transmission Electron Microscopy (TEM)	8
5.3.	Energy Dispersive X-ray analysis (EDX)	8
5.4.	X-Ray Diffraction analysis (XRD)	9
5.5.	Fourier Transform Infrared Spectroscopy (FTIR)	9
6.	Applications	9
6.1.	Separation of metal ions	9
6.2.	Photocatalytic activity	9
6.3.	Antimicrobial activity	10
6.4.	Major equipment and lab facilities required	10
7.	Thesis outline	11
8.	Refrences	11

1. Introduction

Urbanization and industrialization accelerate the immense production of different inorganic and organic substances [1]. These substances contain metallic residues from metallurgical processes and colored substances produced as waste from textile, pharmaceutical, cosmetic and plastic industry [2, 3]. The discharge of these organic and inorganic impurities results environment deterioration by degrading natural resources including water, air and soil [4]. A number of physical, electro-chemical, biological and chemical methods has been explored for the exclusion of toxins from water including membrane filtration [5], reverse osmosis [6], adsorption [7], chemical precipitation [8], coagulation, flocculation [9], chemical deposition technique, ion exchange, cementation [10], electrodialysis and electrochemical membrane reduction [11].

Out of all these routes of water treatment, ion exchange technique has been found superior due to its inimitable nature like less expensive, more efficient and do not produce secondary pollutants [12]. Ion-exchange is a physio-chemical reaction which involves exchange of different ions of same charge in solution with free mobile ions of the ion exchange material. In this there is contact between the exchanger and medium in which ions has been exchanged [13]. Polystyrene based compounds are much in use and can be categorized into organic, inorganic and composites. Organic exchangers can be cation exchangers, anion exchangers and amphoteric materials. They have high ion exchange capacity, uniform chemical stability and reproducibility [14-16]. Inorganic exchangers include salts of polyvalent metals, hydroxides, oxides and metal ferrocyanides. These materials have good stability at high temperature and high degree of selectivity [17-19]. Composites or organic-inorganic hybrid ion exchangers involves the mixing both moieties i.e. organic and inorganic. These materials have improved reproducibility, selectivity as well as good chemical, physical and thermal properties [20]. But synthetic polymers have toxic environmental effects due to their time consuming synthesis process, toxicity and low rate of degradation [21]. Now a day, biopolymers based nanocomposites has been highly favorable in contrast to petroleum based polymers for the sustainable development [22].

Biopolymers have admirable characteristics including inexpensiveness, biodegradability, biocompatibility, non-toxicity, and abundant availability. Polymers like protein, cellulose, starch, pectin, chitin, xyloglucan etc are obtained from natural resources [23, 24]. There are severe expansions in the properties of ion exchangers by using different modifications routes like

synthesis of composite by incorporating organic polymer into the matrix of inorganic precipitate and shifting from bulk material to nano scale composite [25, 26]. Also, biopolymers can be modified into different shapes like rod [27], sheet [28] and gel [29] and used for various applications like heavy metals separation [30], antimicrobial nature [31], photocatalytic activity [32], electrochemical devices [33] and electric membranes [34].

2. Literature Review

Ion exchange is the process of removing out of an ion from aqueous solution which is substituted by other ionic species. It involves contact between the exchanger and medium in which the exchange occurs. In nature, the process of nitrogen uptake by plants is one of the examples of ion exchange. Some of the early instances of the use of ion exchange by humans dated back to Aristotle, who in his book *Problematica* stated that sand filters were used for the purification of sea and impure drinking waters. In 1947, American Chemical Society in its symposium reported for the first time the capabilities of ion exchange technique.

In 1973, Grieves et al studied the distribution coefficient for the exchange of nitrate, iodide and bromide anions by the use of quaternary ammonium surfactant, EDTA which act as cationic surfactant [35].

In 1982, Szepesi et al proposed a novel chiral ion exchanger for the enantiomeric separation of alkaloids with good selectivity and separation efficiency. The system has no sensitivity to the water content of the solvents used for eluent preparation [36].

In 1997, Samczynski et al prepared amphoteric ion exchanger resin Retardion 11A8 and chelating ion exchanger chelex 100 for inorganic ion separation [37].

In 2001, Anasthas et al studied acetic acid sorption from non aqueous solvents ethyl acetate and ethanol by using polymeric resin of styrene-divinyl benzene copolymer. The functional groups of resin form hydrogen bond with the acid which helps in the effective and selective uptake of acid from non aqueous solvent [38].

In 2005, Chubar et al synthesized double hydrous oxide ($Fe_2O_3.Al_2O_3.xH_2O$) ion exchanger by sol-gel method and used for the adsorption of F^-, Cl^-, Br^- and BrO_3^- in different pH environments. The optimal range for adsorption of anions was 3-10 [39].

In 2006, Nilchi et al reported the preparation of cerium (IV) molybdate cation exchanger at different ph. The prepared cation exchanger show high selectivity and excellent absorption of ions [40].

In 2009, Jawor et al prepared linde type A zeolite crystal via hydrothermal and microwave heating methods and compared their physical and chemical properties like crystal size, synthesis time, ionic nature, solubility. Crystal showed fast ion exchange kinetics and high binding capacity for divalent metal ions [41].

In 2010, Nabi et al prepared a composite cation exchange material n-butylacetatezirconium(IV) iodate and checked its sorption behavior towards heavy metal ions in different solvents including orthophosphoric acid, ethyl acetate, dimethylformamide and dimethylsulphoxide etc. It can retain ion exchange capacity upto 200℃ [42].

In 2016, Pathania et al reported lactic acid-Zr(IV) phosphate nanocomposite by sol-gel method and employed for ion exchange capacity, photocatalytic degradation of pollutant. Nanocomposite showed 89% of degradation of methylene blue with regression coefficient of 0.96 [43].

In 2017, Cardoso et al used the dealgenated seaweed waste from brown algae *Sargassum filipendula* in the removal of toxic metals from waste water. Different metal ions like Ag^{+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, Zn^{2+} were evaluated with the biomass. Out of all, for cadmium and chromium it shows maximum ion exchange capacity with sodium ion. The biomass was explored as biosorbent for the removal of toxic metal ions [44].

In 2017, Pathania et al reported the preparation of alginate-Zr(IV) phosphate nanocomposite by sol-gel method as ion exchanger to be used in heavy metal separation, exclusion of organic and microbial impurities from aqueous system. Nanocomposite was highly selective to Al^{3+} and Mg^{2+}. It has been recorded that 90% of pollutant was removed by the nanocomposite by following pseudo-first order kinetics [45].

In 2017, Sharma et al prepared Gd-cl-poly(AAm)-Zr(IV) iodooxalate composite by combining inorganic matrix into polymeric mixture under fixed conditions. The synthesized ion exchanger was then analyzed for ion exchange capacity under different conditions of reaction parameters [46].

In 2017, Thakur et al by using sol-gel method prepared gelatin-Zr(IV) phosphate ion exchanger and used it in separation of metal ions [47].

In 2018, Maltseva et al synthesized nanocomposite consisting of styrene-divinylbenzene matrix incorporated with zirconium dioxide to act as anion exchange composite for arsenate ion. Addition of zirconium dioxide into matrix provided good sorption results of the composite [48].

In 2019, Kumar et al by using sol-gel process prepared polyacrylamide stannic arsenate nanocomposite to act as ion exchanger. The prepared nanocomposite show good physiochemical properties as compared to inorganic part. It also shows photocatalytic properties by degrading 86.22% of sunset yellow dye in 3h of exposure [49].

In 2019, Imaan et al synthesized titanium dioxide and poly vinyl alcohol based nano composite ion exchange membranes for methanol based fuel cell applications. The prepared membrane was compared with, commercially available membrane (nafion 117) and the former show better results in terms of water uptake and methanol uptake capacity [50].

3. Objectives

1. To synthesize biopolymer based nanocomposites.
2. To characterize bionanocomposites using different techniques like SEM, TEM, XRD, EDS, TGA, FTIR and UV-VIS.
3. To study the ion exchange behavior of the bionanocomposites.
4. To study the distribution coefficient of different metal ions.
5. To study the photocatalytic activity of bionanocomposites for the exclusion of different pollutants.
6. To study antimicrobial activity of bionanocomposites against different bacteria.

4. RESEARCH METHODOLOGY

4.1. EXTRACTION OF XYLOGLUCAN FROM TAMARIND SEED

Tamarind seeds will be soaked in water to remove outer brown coat. The seed kemels will dried and grinded to make powder as stock. 20g of powder from stock will be added into 200 ml of distilled water and slurry will be formed. The slurry will be added into boiling water with constant stirring for 20 min. The resulted clear solution will be allowed to stand overnight. Centrifugation will be done to the upper clear part and to rest absolute alcohol will be added with

continuous stirring. The precipitate formed will be washed with ethanol, ether and dry at 60ºC [51].

4.2.SYNTHESIS OF ZIRCONIUM(IV) SELENOPHOSPHATE (ZSPT) INORGANIC ION EXCHANGER

Zirconium(IV) selenophosphate will be prepared by adding 0.1N sodium selenite, 0.1N zirconium oxychloride octahydrate and 0.1N orthophosphoric acid in volume ratio (1:2:1) with continuous stirring at 60˚C. The pH of solution will be adjusted to 0-1 by adding either the dilute solution of ammonia or hydrochloric acid. The resulting precipitate will kept overnight in the mother liquor to settle down and then filtered. The excess of acid will be removed by washing the precipitates with double distilled water and dried at 60˚C.

4.3.SYNTHESIS OF ZIRCONIUM(IV) ALUMINOPHOSPHATE (ZAP) INORGANIC ION EXCHANGER

In this, zirconium(IV) aluminium phosphate will be prepared by adding 0.1N aluminium sulphate, 0.1N zirconium (IV) oxychloride octahydrate and 0.1N orthophosphoric acid in volume ratio (1:2:1) with constant stirring at 60˚C. The pH of solution will be adjusted to 0-1 by adding dilute solution of ammonia or hydrochloric acid. The resulting precipitate will be kept overnight in the mother liquor to settle down and then filtered. The excess of acid will be removed by washing the precipitates with double distilled water and dried at 60˚C.

4.4.SYNTHESIS OF CAROB GUM BASED BIONANOCOMPOSITE

Carob gum/zirconium(IV) selenophosphate (CG@ZSPT) bionanocomposite will be prepared by adding 0.1N sodium selenite, 0.1N zirconium (IV) oxychloride octahydrate and 0.1N orthophosphoric acid in volume ratio (1:2:1) with constant stirring at 60˚C. The pH of resulting mixture will be adjusted to 0–1 by adding diluted hydrochloric acid. The mixture will be stirred for 2h with continuous stirring. Fixed amount of carob gum will be added to mixture of inorganic part with continuous stirring. The resultant mixture will be stirred for 2h on the magnetic stirrer at fixed temperature. The precipitates will be filtered and washed with double distilled water for further purification. The precipitates obtained will be dried at 60˚C. In this way, a number of samples have been prepared by different compositions of organic part [46].

4.5.**SYNTHESIS OF XYLOGLUCAN BASED BIONANOCOMPOSITE**

Xyloglucan/zirconium(IV) selenophosphate (XG@ZSPT) bionanocomposite will be prepared by adding 0.1N sodium selenite, 0.1N zirconium (IV) oxychloride octahydrate and 0.1N orthophosphoric acid in volume ratio (1:2:1) with constant stirring at 60˚C. The pH of resulting mixture will be adjusted to 0–1 by adding diluted hydrochloric acid. The mixture will be stirred for 2h with continuous stirring. The precipitates of xyloglucan will be added to mixture of inorganic part with continuous stirring. The resultant mixture will be stirred for 2h on the magnetic stirrer at room temperature. The precipitates will be filtered and washed with double distilled water to eliminate impurities and precipitates obtained will be dried at 60˚C. In this order, a number of samples has been prepared by varying the concentration of organic part [46].

4.6.**SYNTHESIS OF CAROB GUM-cl-XYLOGLUCAN BASED BIONANOCOMPOSITE**

Carob gum-xyloglucan/zirconium(IV) selenophosphate (CG-XG@ZSPT) bionanocomposite will be prepared by adding 0.1N sodium selenite, 0.1N zirconium (IV) oxychloride octahydrate and 0.1N orthophosphoric acid in volume ratio (1:2:1) with constant stirring at 60˚C. The pH of resulting mixture will be adjusted to 0–1 by adding diluted hydrochloric acid. The precipitates of carob gum and xyloglucan will be added to mixture of inorganic part with continuous stirring along with calculated amount of glutaraldehyde. The resultant mixture will be stirred for 2h on the magnetic stirrer at room temperature. The precipitates will be filtered and washed with double distilled water to eliminate the impurities. The precipitates of carob gum-xyloglucan/zirconium(IV) selenophosphate (CG-XG@ZSPT) obtained will be dried at 60˚C. In this order, a number of samples have been prepared by varying the composition of organic part [25].

4.7.**SYNTHESIS OF CAROB GUM-cl-PSYLLIUM HUSK BASED BIONANOCOMPOSITE**

Carob gum-psyllium husk/zirconium(IV) aluminophosphate (CG-PSK@ZAP) bionanocomposite will be prepared by adding 0.1N aluminium phosphate, 0.1N zirconium (IV) oxychloride octahydrate and 0.1N orthophosphoric acid in volume ratio (1:2:1) with constant stirring at 60˚C. The pH of mixture will be adjusted to 0–1 by adding diluted hydrochloric acid. The precipitates of carob gum and psyllium husk will be added to mixture of inorganic part with continuous stirring along with calculated amount of glutaraldehyde. The resultant mixture will be stirred for 2h on the magnetic stirrer at room temperature. Now, obtained precipitates will be filtered and

washed with double distilled water to eliminate impurities. The precipitates of carob gum-psyllium husk/zirconium(IV) aluminophosphate (CG-PSK@ZAP) obtained will be dried at 60˚C. In this way, a number of samples have been prepared by varying the composition of organic part [25].

4.8.**ION EXCHANGE CAPACITY**

Synthesized composite material will be explored to study the ion exchange capacity (IEC) by using column process [47]. in this process, fixed amount of bionanocomposite will be placed in a glass column fitted with glass wool. Firstly, the ion exchange column will be washed with distilled water to remove impurities if any present. After that 0.1 N solution of sodium chloride will be passed through the column with flow rate of 15-20 drops per min. Then, obtained effluent will be titrated with base using indicator. The ion exchange capacity will be determined by using formula:

$$\mathrm{IEC} = \frac{\mathrm{N} \times \mathrm{V}}{\mathrm{W}}$$

Where N = Normality of alkali

V = Volume of alkali

W = Weight of composite

4.9.**DISTRIBUTION COEFFICIENT STUDIES**

The distribution coefficients of different metals onto ion exchanger will be obtained by using batch method as studied in literature [47]. In this, 200 mg of ion exchange material (in H^+) will be added into different metal nitrates (20 mL) taken in different beakers. The above mixture will be placed for 24 h with continuous stirring in order to attain equilibrium. Further the amount of different metal ion solutions will be calculated by titrating it against ethylenediaminetetraacetic acid.

$$\mathrm{K_d} = \frac{\mathrm{I}-\mathrm{F}}{\mathrm{F}} \times \frac{\mathrm{V}}{\mathrm{M}}\ \mathrm{mL/g}$$

Where I = Initial volume of metal ion solution

F = Final volume of metal ion solution

V = Volume of solution

M = Amount of composite

4.10. **OPTICAL BAND GAP STUDIES:**

In this, a suspension of nanoparticles (5mg) will be prepared in ethanol [49]. Then the above suspension will be ultrasonicated for 20 min and UV-Visible spectrum will be recorded. The band gap of the synthesized material will be computed by using Tauc relation:

$$\alpha = B(h\nu - E_g)n$$

Where α = absorption coefficient

hν = photon energy

B = band tailing parameter

E_g = band gap

n = 1/2 for direct band gap semiconductors.

The optical band gap will be obtained by extrapolating the straight line to portion of the curve between $(\alpha h\nu)^2$ and hν when α = 0.

5. CHARACTERIZATION TECHNIQUES

5.1.Scanning Electron Microscopy (SEM)

The scanning electron microscopy studies will made on scanning electron microscope to determine the morphology of particles. This technique provides images of a sample by scanning it using high energy electron beams. Then the electrons will interact with atoms of the sample and producing signals which reveal information about the sample composition, surface topography and other properties such as electrical conductivity.

5.2.Transmission Electron Microscopy (TEM)

TEM construct a high resolution, black and white image from the interaction that takes place between samples and energetic electrons in the vacuum chamber. It provide information including compositional, morphological, crystalline and topographical. TEM micrographs yields information of shape, size, structure and features of the sample.

5.3.Energy Dispersive X-ray analysis (EDX)

EDX is used for the elemental analysis of a sample by analysing X-rays emitted from the specimen when bombarded by the electron beam. This technique employs rays of different wavelengths ranges from 10 to 0.01 nm. It is used to identify as well as measure the concentration of elements.

5.4.**X-Ray Diffraction analysis (XRD)**

XRD pattern provides information about crystalline phase of the materials as well as the crystallite size. The average particle size of synthesized materials was obtained from XRD measurement value of FWHM (Full Width at the Half Maximum Intensity) using Debye-Scherrer's formula given in following equation.

Scherrer's equation $D = \frac{K\lambda}{B\cos\theta}$

Where K = constant (0.9)

λ = wavelength (λ=1.54 Å)

β = full width at the half maximum intensity (FWHM)

θ = half diffraction angle.

5.5.**Fourier Transform Infrared Spectroscopy (FTIR)**

FTIR analysis is carried in the range 400 cm^{-1} to 4000 cm^{-1} by using infrared spectrophotometer. FTIR spectroscopy can be used to identify the structure of unknown composition or its chemical group. The intensity of absorption spectra associated with molecular composition of the chemical group.

6. APPLICATIONS

6.1.**Separation of metal ions**

In this process, 200 mg of bionanocomposite will be added to 20 ml of different metal ion solution prepared in double distilled water. Different metal pairs will be passed through ion exchange column several times in order to adsorb metal ions on bionanocomposites. After that column will be washed with distilled water and adsorb metal ions will be eluted using different solvents. Further, percentage of metal ion in solution before and after equilibrium will be attained by titrating with EDTA [49].

6.2.**Photocatalytic activity**

The photocatalytic degradation efficiency of synthesized bionanocomposites will be examined against different pollutants. Initially, different parameters including concentration of pollutant, bionanocomposite dosage, time and pH etc. will be optimized. Different sets with optimized parameters will explored by maintaining total volume of reaction mixture to 50 mL. Further the

mixture of pollutant and bionanocomposite will be kept in dark to achieve adsorption-desorption equilibrium. Then the mixture will be subjected to sunlight and 5 mL of aliquot will be taken out at different time intervals. The above aliquot will be centrifuged to remove nanoparticles and absorbance will be noted in 200 to 700 nanometer range [32].

The percent degradation of dye will be calculated using formula as

$$\% \text{ Degradation} = \frac{C_o - C_t}{C_o} \times 100$$

Where C_0= initial concentration

C_t= instant concentration at any time t of organic pollutant.

The kinetics of degradation will be elaborated by using Pseudo first order kinetics. The rate constant (k) will be determined using Eq. as given below:

$$k = 2.303 \times \text{slope}$$

Where slope will be calculated from the plot of ln(absorbance)versus t.

6.3.**Antimicrobial activity**

Colony of given bacteria will be collected from the overnight nutrient agar plate culture and transferred into 10 mL nutrient broth (NB) in a conical flask. The above assembly will be incubated at 37˚C for 24 h with 100 rpm. The above culture will be diluted for 5 – 10 colony forming unit/mL with nutrient broth. Now, diluted culture (5mL) will be pipette out into different conical flasks containing nutrient broth (95 mL). Four different concentrations of bionanocomposite will be added into these flasks and incubated at 37˚C for 24 h with 100rpm. Optical density of each sample will be analyzed after every hour by using spectrophotometer [19].

6.4.**Major equipment and lab facilities required**

The major equipment's required for this research work will be X-ray diffractrometer (XRD), Thermogravimetric analysis (TGA), Scanning electron microscope (SEM), Transmission electron microscope (TEM), Fourier transform infra-red (FTIR) spectroscopy, Energy-dispersive X-ray (EDX) spectroscopy and UV-visible spectrophotometer. All the primary lab facilities and some major instruments including muffle furnace, autoclave, sonicator, magnetic stirrer, hot plate and UV-vis spectrophotometer are acknowledged from IEC University. The other instruments required in present research work will be availed from different institutes.

7. THESIS OUTLINE

Chapter 1: Introduction

Introduction part contains pollutants, types, sources and methods used for their removal using biopolymer based nanocomposite ion exchangers in detail.

Chapter 2: Literature Review

Literature Review includes history, preparation of novel ion exchange materials and their applications in different fields.

Chapter 3: Experimental techniques

Experimental part account for different routes for the synthesis of bionanocomposite ion exchanger with different characterization techniques used in current research work.

Chapter 4: Results and Discussion

In this part, different experimental results related to synthesis, characterization, ion exchange properties and applications of novel bionanocomposite ion exchangers will be elaborated.

Chapter 5: Summary and Conclusion

This chapter sum up our research work briefly and extend significant results achieved from the research work.

Chapter 6: References.

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RESEARCH SCHOLAR

Ajay Sharma

Research Scholar

Registration Number: H18IECPHD02

Department of chemistry

IEC University,Baddi(HP),India.

SUPERVISOR

Dr Manita thakur

Assistant Professor

Department of chemistry

IEC University,Baddi(HP),India.